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<b>(54) Title:</b> SILICON CARBIDE GRAIN <b>(57) Abstract</b> <p>A sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon.</p>		

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## SILICON CARBIDE GRAIN

## BACKGROUND OF THE INVENTION

Silicon carbide abrasive grain typically is produced by the well known Acheson process. In this process, silica sand and petroleum coke are packed around a  
5 conductive graphite core which is resistively heated with an electric current. During heating to the high temperatures achieved within the packed bed, the reaction of carbon and silica results in the formation of a silicon carbide ingot. This ingot is separated from the  
10 graphite core and unreacted sand and subsequently crushed into useful shapes and sizes to produce conventional silicon carbide grain. The quality of the silicon carbide grain made from this process is determined by the purity of the feed material, the method of packing the  
15 furnace feed bed, the temperature history followed in the firing cycle, and the crushing and post treatments used in producing grains.

In the Acheson process, graphite, silicon metal, silica, metallic carbides and other oxide mineral phases  
20 are typically formed as reaction byproducts in the furnace bed. These contaminant phases are codeposited and entrained within the silicon carbide which is the primary reaction product produced in the furnace. Thus, the quality of silicon carbide grain produced by this  
25 process is also generally dependent on the presence and elimination of extraneous phases and contaminants during the subsequent processing operations of crushing, sizing, floatation, chemical treatment and washing.

As mentioned above, one factor which influences the  
30 quality of conventional silicon carbide grains is the mechanical crushing operations which are required to reduce the size of the massive silicon carbide crystals which form in the Acheson furnace to useful grit sizes used in abrasive products. The severe mechanical forces

required for crushing large silicon carbide crystals into useful grit sizes introduce dislocations and microcracks as defects in conventional silicon carbide grain. These defects, as well as any inclusions of the residual  
5 contaminant material phases from the furnacing operation, act as characteristic flaws which tend to degrade the hardness, toughness and strength of conventional grains which are generally monocrystalline.

When used in grinding wheels, the conventional  
10 silicon carbide abrasive grains produced by the above process exhibit certain deficiencies. Because these monocrystalline grains are intrinsically brittle in nature, they fracture under normal grinding loads, leading to catastrophic cleavage of the grain and  
15 accelerated removal of grain material from the grinding wheel during use. Inclusions of other phases and the mechanical crushing operations used in producing conventional grains introduce crystal defects and flaws in these grains which tend to weaken the material further  
20 and compromise its performance in grinding applications. Inclusions of contaminant phases may also increase the reactivity of the grain to the workpiece during grinding of certain materials and further degrade grinding performance due to chemical reactions between the grain  
25 and workpiece. In addition, conventional silicon carbide grains produced by the Acheson process typically have a smooth surface texture due to the fracture and cleavage of monocrystals during the crushing operation. This smooth surface texture prevents effective bonding of the  
30 grain and matrix phase in most abrasive products and promotes grain pullout and accelerated wheel wear during grinding operations.

The prior art has attempted to improve upon the conventional monocrystalline silicon carbide grains  
35 produced by the Acheson process by other processing routes. For example, U.S. Patent No. 3,480,395 (McMullen et al.) extrudes a green body of fine silicon carbide

powder, excess carbon and a temporary binder, and fires it in the presence of free silicon to produce a polycrystalline, siliconized silicon carbide grain. However, the grain produced by this process suffers from many deficiencies. In particular, the presence of free silicon in the final grain increases the reactivity of the grain toward most alloy materials, makes the grain susceptible to undesirable oxidation in a typical grinding application environment, decreases the hardness of the grain and severely degrades the grain's grinding performance at the high temperatures encountered at the abrasive-workpiece interface.

Thus, it is an object of the present invention to produce a silicon carbide grain having improved mechanical and chemical properties for abrasive applications.

#### SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon. In some embodiments of the present invention, the silicon carbide abrasive grain has a textured surface.

Also in accordance with the present invention, there is provided a process for producing silicon carbide grains comprising the steps of:

- a) forming a shape from a formulation comprising silicon carbide powder,
- b) crushing the shape to produce silicon carbide grains, and
- c) sintering the grains either before or after crushing the shape.

In further accordance with the present invention, there is provided either a composite or an abrasive article, including but not limited to, a coated abrasive, a grinding wheel, a lapping compound, an abrasive pad, and an abrasive fabric, comprising the silicon carbide abrasive grains.

## DESCRIPTION OF THE FIGURES

Figures 1-3 are photographs of textured surfaces of abrasive grains of the present invention.

Figure 4 presents properties of the abrasive grains of the present invention and comparative example grains.

Figure 5 presents vitrified grinding wheel properties for the abrasive grains of the present invention and comparative example grains.

Figure 6 presents grinding wheel performance data for the abrasive grains of the present invention and comparative example grains.

## DETAILED DESCRIPTION OF THE INVENTION

The formulation comprising silicon carbide powder and at least one sintering aid usually includes conventional additives. Typically, the formulation comprises sintering aids and temporary binders, and may also include dispersants, surfactants, humectants, plasticizers, fungicides and mold release agents. In a preferred embodiment of the present invention, the formulation consists essentially of silicon carbide powder, at least one sintering aid, a binder and water.

The silicon carbide powder of the present invention may be in the alpha form, the beta form, or a mixture thereof. In addition, the form of silicon carbide powder may be either of a green, high purity type or a black, low purity type or mixtures thereof. In preferred embodiments, the alpha form of silicon carbide powder is used. The particle sizing of the powder must be small enough to insure the sinterability of the formulation. Hence, the mean diameter of the silicon carbide powder is typically between about 0.01 and about 3 microns, preferably between about 0.5 and about 1.0 microns, and most preferably about 0.7 microns. Typically, the surface area of the powder is between about 5 and about 50 M<sup>2</sup>/g, preferably about 10 to 15 M<sup>2</sup>/g. In practicing the present invention,  $\alpha$ -silicon carbide powders such as

Norton FCP-10 or FCP-15, manufactured by Norton A/S in Lillesand, Norway; Stark A10 or A20, manufactured by Hermann C. Starck, Inc. of New York, NY; and Lonza UF10 or UF20, manufactured by Lonza of Fair Lawn, NJ, may typically be used.  $\beta$ -SiC powders or mixtures of  $\alpha$ -SiC and  $\beta$ -SiC powders may also be used as a starting material. In preferred embodiments, Norton FCP-15  $\alpha$ -SiC powder is used. The amount of silicon carbide powder used in the formulation of the present invention generally constitutes between about 60% and about 99% by weight of the formulation, preferably between about 90% and about 98%, and more preferably about 97%.

If it is deemed desirable to reduce the size of coarse silicon carbide starting materials to promote sinterability, these materials can be milled to a mean particle size of less than about one micron. This milling can be performed in water not only in the absence of organic solvents which protect the silicon carbide from oxidation, but also without subsequent chemical treatments to remove oxidized silicon carbide or other contaminants. In preferred embodiments, there is provided a process for producing a sintered silicon carbide ceramic comprising the sequential steps of:

- a) milling an aqueous slurry of coarse silicon carbide powder at a predetermined pH value of between about 6.0 and about 10.0 to reduce the mean particle size of the silicon carbide powder to less than one micron,
- b) adding at least one sintering additive to the aqueous silicon carbide powder slurry,
- c) homogeneously mixing the sintering additive with the aqueous silicon carbide slurry,
- d) drying the milled slurry to a moisture content of less than about 30% by weight of the silicon carbide powder,
- e) forming a green body from the dried slurry, and
- f) sintering the green body without subjecting the

green body to chemical treatments which remove oxygen or other impurities.

In preferred embodiments, the milled slurry is dried to produce a concentrate with a moisture content of less than 2% by weight of the silicon carbide powder.

In many embodiments of the present invention, a plurality of sintering aids are used. Preferred sintering aids include boron-based aids and carbon-based aids. However, use of oxide-based aids such as CaO, MgO, BaO, alkaline earth, transition metal or rare earth oxides as sintering aids is also contemplated to be within the scope of the present invention. These sintering aids may be used alone, in combination with one another or together with alumina, silica, phosphate or borate additions. The use of metals, metal carbides, borides, aluminides, silicides, phosphides or combinations of metals, carbides, oxides, aluminates, silicates, phosphates, borates, aluminides, silicides, phosphides and borides as sintering aids is also contemplated to be within the scope of the present invention.

In preferred embodiments of the present invention, the formulation comprises a carbon-based aid and a boron-based aid. The carbon-based aid of this preferred formulation is typically either an organic resin, more preferably Al-5614 resin, manufactured by Borden Industrial Resins of Louisville, KY, or carbon black, more preferably Regal 400 carbon black, manufactured by Cabot Corporation of Billerica, MA. The carbon-based aid typically comprises between about 0.5% and 20% by weight of the formulation of the present invention, preferably between about 1% and about 10%, more preferably between about 2% and about 6%.

The boron-based aid is typically boron carbide or elemental boron, preferably Starck HS Boron Carbide, manufactured by Hermann C. Starck, Inc. of New York, NY. This aid typically comprises between about 0.1% and 30%



by weight of the formulation of the present invention, preferably between about 0.5% and about 10%, more preferably between about 0.5% and about 5%.

5 In some formulations of the present invention, the amounts of the boron-based aid and the carbon-based aid are substantially greater than conventional usage. In these embodiments, the boron-based aid is present in an amount of between about 4 w/o and about 30 w/o of the formulation, preferably between about 4 w/o and about 10  
10 w/o, more preferably between about 4 w/o and about 6 w/o, while the carbon-based aid is present in an amount of between about 6 w/o and about 10 w/o of the formulation, preferably between about 6 w/o and about 8 w/o, more preferably between about 6 w/o and about 7 w/o.

15 Temporary binders used in accordance with the present invention typically include polyvinyl alcohol (PVA), paraffin wax, polyethylene glycol (PEG), starch or cellulose derivatives, and preferably are either Goshenol KH-17S PVA (manufactured by Nippon Gohsei, Osaka, Japan),  
20 Elvanol 75-15 PVA (manufactured by DuPont Polymers, Wilmington, DE) or Carbowax 400 PEG (manufactured by Union Carbide Corp., Danbury, CT). This additive typically comprises between about 0.1% by weight ("w/o") and about 10 w/o of the formulation of the present  
25 invention, preferably between about 0.25 w/o and 5 w/o.

The formulation comprising silicon carbide powder and at least one sintering aid can be prepared by any conventional method. For example, the formulation's components can be simply mixed in a solvent such as water  
30 to form a homogeneous formulation with a predetermined solids loading which is ready for forming. Typically, however, the silicon carbide powder is mixed overnight in a jar roll mill with a pH-adjusted mixture of the sintering aid, binder and water, wherein the pH is  
35 adjusted to between 8.0 and 9.0 by addition of ammonium hydroxide. Following initial mixing, the formulation can be subjected to a filtration, spray drying, freeze drying

or oven drying step which removes water from the formulation. Typically, the formulation is spray dried in a Niro HT spray drier (Niro Inc., Columbia, MD) which produces discrete, homogeneous spherical powder  
5 agglomerates which create a flowable powder media amenable to further processing and forming of green bodies.

If a green body is formed from the formulation prior to sintering, that green body can be made by any  
10 conventional forming method. For example, the formulation can be slip cast, injection molded, dispersion cast, tape cast, sprayed, atomized, nebulized, or agglomerated in a mixer, extruded, cold uniaxially pressed or cold isostatically pressed to form the green  
15 body.

In one embodiment of the present invention, the powder formulation is spray dried and the resulting spherical agglomerates are sintered to produce dense  
20 spherical grains of fine diameter, ranging in size from 2 um to 250 um diameter, where grain size distribution is controlled by adjusting the spraying conditions in the spray drier.

In another embodiment of the present invention, the spray dried powder formulation is subsequently pelletized  
25 in an R07 Eirich mixer (Eirich Machines Inc., Maple, Ontario, Canada). The Eirich mixer offers process control advantages in that it can mix both dry and wet powders and produce a narrow pellet size distribution by simple adjustment of mixer operating conditions. The  
30 powder formulation, which is fed into the mixer with additions of water and binder, agglomerates into small seed-like fractions which further agglomerate to larger sized aggregates to produce dense green pellets ranging in diameter from about 0.1 mm to about 10.0 mm and  
35 typically having densities in the range of 1.5 to 2.0 g/cm<sup>3</sup>.

In another typical method of green body formation,

the spray dried powder formulation is mixed with water, binder, plasticizer, humectant and a mold release agent to a plastic-like consistency in an Abbe MF sigma-blade mixer (Paul O. Abbe Inc., Little Falls, NJ) and fed into  
5 an extruder to produce extruded green bodies. The geometric shape of the die orifice of the extruder can be circular, elliptical, annular, triangular, quadrilateral, diamond, square, rectangular, trapezoidal, hexagonal, pentagonal, corrugated, hollow or any other geometric  
10 shape. The selected shape will be transferred to the powder extrudate during the extrusion process and typically will not vary over the length of the extrudate. Since the orifice of the extruder is typically a circle, the extruded green body is typically a cylinder. In the  
15 preferred embodiment of the present invention, the extruder is either a piston extruder or a twin screw extruder although other types of extrusion equipment can be suitably used. The diameter of the extruded green body, i.e., the longest distance measured across the face  
20 of the orifice, is typically between about 1 to 1000 microns, preferably between about 1 and about 20 microns, more preferably between 1 and 5 microns. The length of the extruded body is typically between about 10 and about 10,000 microns, preferably between about 1.0 and about  
25 5.0 microns. These extruded green bodies typically have densities in the range of 1.5 to 2.0 g/cm<sup>3</sup>.

In yet another embodiment, the spray dried powder formulation is cold isostatically pressed ("CIPed") to produce green billets or bricks. Typically, this is  
30 performed at a pressure of between about 10,000 and about 50,000 psi, preferably about 30,000 psi. These billets may assume any shape but commonly take the form of rectangles or squares. In preferred embodiments of the invention, an ISOMAX-30 cold isostatic press,  
35 manufactured by National Forge Co. of Irvine, PA is used. Typically, the CIPed green body has a width of between about 7.5 cm and about 15 cm, a length of between about

7.5 cm and about 15 cm, a depth of between about 1.0 and about 4.0 cm, and a density in the range of 1.5 to 2.0 g/cm.

5 In some embodiments of the present invention, the green bodies are crushed then sintered. This sequence of processing produces a controlled textured surface on each sintered grain. This textured grain provides for superior grain-matrix bonding, superior abrasive wheel strength, hardness and toughness and hence superior  
10 grinding performance where abrasive-matrix adhesion is important. In one preferred embodiment of the present invention, the formulation of the present invention is extruded to produce a green extrudate, then the extrudate is crushed, and then sintered. In another preferred  
15 embodiment, the formulation is cold pressed to produce tiles, the tiles are then crushed then sintered. In yet another embodiment, the formulation is agglomerated to form pellets which are then crushed and sintered.

In some embodiments of the present invention, the  
20 green bodies are sintered then crushed. This sequence of processing produces a grain having a smooth surface texture. In one preferred embodiment of the present invention, the formulation of the present invention is extruded to produce a green extrudate which is sintered  
25 and then crushed. In another preferred embodiment, the formulation is cold pressed to produce tiles. The tiles are then sintered and crushed. In yet another embodiment, the formulation is agglomerated to form pellets which are then sintered and crushed.

30 The crushing step of the present invention breaks down the green or sintered intermediate shaped bodies of the present invention into polycrystalline grain shapes of suitable grit sizing and shape for a variety of abrasive applications. It can be performed by any  
35 conventional crushing machine, including, but not limited to, jaw crushers, impact mills, jet mills, roll mills and rod mills. In a preferred embodiment for producing

sharp, high aspect ratio shaped grains, the shaped bodies are crushed into grains by an 8" by 5" laboratory roll crusher, manufactured by Sturtevant Co. in Boston, MA. However, in a preferred embodiment for producing grains of a predetermined cross sectional shape, where the crushing step is typically limited to fracturing the shaped body at a predetermined length in order to produce a uniform aspect ratio, the fracturing of grains having predetermined cross sectional shapes is commonly performed with an impact mill.

The crushing of the shaped bodies typically results in polycrystalline silicon carbide grains of either highly irregular shapes or predetermined cross sectional shapes. Each grain, however, can be characterized by a length and a diameter. The length of the grain is defined as the longest straight-line distance present in the grain while the diameter is defined as the longest straight line distance perpendicular to the "length" axis of the grain. The ratio of the length to the diameter of any particular grain is known as the "aspect ratio" of the grain. Grains having an aspect ratio greater than about 1.5 are referred to as "weak" shaped grains. Grains having an aspect ratio of less than about 1.5 are known as "blocky" shaped grains while grains having an aspect ratio of between about 1.0 and about 1.2 are known as "strong" shaped grains.

The sintering cycles of the present invention promote the development of a desirable microcrystalline grain structure without excessive grain coarsening. Such sintering can be performed by any conventional sintering means, including hot pressing, pressureless sintering, gas pressure sintering, hot isostatic pressing (HIP) and sinter-HIPing. In one embodiment of the present invention, the formulation is fed directly into a hot press, thus bypassing the formation of a green body. When hot pressing is used as the sintering method, the green body is typically sintered at 2100°C for 30 minutes

at 3000 psi ram pressure. When pressureless sintering is used, heating the green grain to 1500°C under vacuum, backfilling with argon gas at 1500°C, heating to a sintering temperature of 2150°C under an argon atmosphere and holding at 2150°C for 15 to 60 minutes in an argon atmosphere is the preferred firing cycle. When gas pressure sintering is used, the green body is commonly soaked at 2100°C for 30 minutes under 3000 psi of argon gas. The preferred hot isostatic pressing method involves sub-jecting the green body to 2100°C for 15 to 60 minutes at a minimum pressure of 3000 psi under argon. Final density, hardness, strength and crystallite size in the sintered grain is influenced by the sintering temperature and time at temperature in the firing cycle. Typically, grain density, hardness and strength increase with increased sintering temperature. Crystallite size in the sintered grain is controlled by the elapsed time at sintering temperature, where increasing the sintering time typically produces coarser crystallites.

In some processes of the present invention, there is provided a process for sintering a silicon carbide blend which has either a moisture content of at least about 0.2 w/o or has an oxygen content of at least about 0.1 w/o, wherein the sintering cycle comprises a first step which drives off moisture, processing additives, organics and the like and a second step which drives off oxygen bound to silicon such as silica and silicates. In preferred embodiments, this process comprises the steps of:

- a) evacuating a furnace containing a sinterable silicon carbide green body having either a moisture content of at least about 0.2 w/o or an oxygen content of at least about 0.1 w/o to a vacuum of at least about 100 torr, more preferably less than about 1 torr,
- b) heating the green body under vacuum to a temperature between about 1000°C and about 1500°,
- c) maintaining the temperature between about 1000°C

- and about 1500°C for at least 30 minutes under vacuum,
- d) backfilling the furnace with argon gas to atmospheric pressure,
  - 5 e) further heating the green body in an argon atmosphere to a temperature between 2000°C and 2200°C,
  - f) maintaining the temperature of between 2000°C and 2200°C for at least 15 minutes in an argon
  - 10 atmosphere, and
  - g) cooling the furnace to room temperature to produce a sintered ceramic.

As mentioned above, when a green body of the present invention is crushed then sintered, a textured grain

15 surface results. This texture of the sintered grain, can be evaluated by comparing either changes in mean surface roughness ( $R_a$ ) or surface area due to a change in topography with a given grit size. When surface roughness is used for characterizing texture, a grain

20 having a mean roughness of greater than 20  $\mu\text{m}$  is considered to have a coarse surface texture. When mean roughness is between 10 and 20  $\mu\text{m}$ , the grain is considered to have a moderate texture. When the mean roughness is between 2 to 10  $\mu\text{m}$ , the grain is considered

25 to have a fine texture. When the mean surface roughness is below 2  $\mu\text{m}$ , the grain is considered to have a smooth, untextured surface. See Figures 1-3, wherein an example of a fine, moderate and coarse textured sintered abrasive grains of the present invention, respectively, are set

30 forth at 500X magnification.

The product produced by the present invention is a sintered, polycrystalline silicon carbide abrasive grain which contains essentially no free silicon. When the product is produced by an extrusion process, the product

35 is called an extruded grain. The size of the crystals in extruded grains typically range from less than one micron to one millimeter. The grain diameter can be controlled

over a range from 10 to 5000 microns, preferably between about 100 and about 1000 microns. The extruded grain aspect ratio typically ranges from between about 1.0 and 1,000, preferably between about 1.0 and about 5.0. The  
5 density of extruded grains commonly ranges from about 88% to about 96% of theoretical density, while its indentation hardness typically ranges between about 18 and about 27 GPa.

When the product is produced by the hot press  
10 method, the product is called a hot-pressed grain. These grains may take on weak, strong or blocky shapes, depending on the preferred shape for the intended application. Because the hot pressed grain is typically crushed after sintering, its surface generally has a  
15 smooth texture. The density of the hot pressed grains is typically between about 97% and about 99% of theoretical density, while its hardness typically ranges between 20 to 29 GPa.

When the green body of the present invention is cold  
20 iso-statically pressed, the sintered grain is referred to as a cold pressed sintered grain. The crystallite size of these grains may be between 1 micron and 1 millimeter. Their densities range from between about 95% to about 99% of theoretical density, while hard-ness is usually  
25 between about 19 and about 26 GPa. The shape of these grains can be controlled by the crushing operation to provide weak, strong or blocky material. When the green body of this em-bodiment is crushed before sintering, the resulting surface is highly textured. When the green  
30 body is sintered prior to crushing, the surface has a smooth texture.

When the green body of the present invention is agglomerated, the sintered grain is referred to as a pelletized grain. The shape and size of the crushed  
35 pelletized grain is typically similar to that of the cold pressed grain. It may have either a textured or smooth surface, depending upon the sequence of the sintering and



crushing operations. Its density is typically between about 95% and about 98% of theoretical density and hardness is usually between 19 to 25 GPa.

Typically, the sintered silicon carbide ceramic  
5 produced from the formulations of the present invention will have boron present in an amount between about 0.1 and about 30 w/o and excess carbon present in an amount of between about 0.1 and about 10 w/o. Ceramics sintered from formulations having higher amounts of sintering aid  
10 will comprise between about 4 and about 30 w/o boron, preferably between about 4 and about 10 w/o, more preferably between about 4 and about 6 w/o; and between about 6 w/o and about 10 w/o excess carbon, preferably between about 6 w/o and about 8 w/o, more preferably  
15 between about 6 w/o and about 7 w/o. "Excess carbon" is defined as the amount of carbon not combined with compounds containing boron as boron carbide or silicon as silicon carbide. In preferred embodiments, these sintered ceramics have a density of at least about 3.00  
20 g/cm<sup>3</sup>. In more preferred embodiments, at least about 50 w/o of the silicon carbide is in the alpha phase and most preferably, at least about 75 w/o of the silicon carbide is in the alpha phase.

The sintered, polycrystalline SiC abrasive grains  
25 which have essentially no free silicon can be incorporated into many abrasive articles either alone, as a direct substitute for conventional monocrystal SiC grains, or in combination with conventional SiC grains or grains of other material compositions. For example, the  
30 grains of the present invention can be used as a loose grit or a lapping compound or can be incorporated into conventional abrasive, coated abrasive articles, or wear articles such as vitrified, resinoid or metallic grinding wheels or stones, coated papers or fabrics, seals or  
35 other shaped abrasive products using the same methods used by the art for attaching or incorporating monocrystalline SiC grains in abrasive articles. The

grains of the present invention can be manufactured in any grit size, although typically between the range of an ANSI 4 grit to a FEPA P1200 grit, with weak, blocky or strong shapes in a variety of surface textures, ranging from coarse to smooth. The abrasive articles having the grains of the present invention can then be used in the same manner as those articles having conventional monocrystalline SiC grains.

The sintered, polycrystalline silicon carbide abrasive grains which have essentially no free silicon can be incorporated into many ceramic, metal, organic polymer or glass matrices as a filler or reinforcement to form composites. The grains of the present invention may be incorporated into such matrices either alone, as a direct substitute for conventional monocrystalline SiC grains, or in combination with conventional grains or fibers of silicon carbide or other material compositions. Composite articles made with grains of the present invention have applications in either abrasive and wear products or structural components where improved hardness, stiffness, strength, wear resistance, thermal conductivity, thermal stability, chemical resistance or friction properties are required.

In order to compare the properties of sintered, polycrystalline silicon carbide grains of the present invention with those of conventional monocrystalline silicon carbide grains, grain characterization testing was performed on individual grain examples. Grain densities, crystallite size and mechanical properties such as grain friability, impact toughness, indentation toughness, hardness and compressive strength were selected as the appropriate measures for comparison. The test methods utilized for determining these properties are described below.

Grain friability is measured with a DeBeers Mark IV Friatester provided by DeBeers Industrial Diamond Division. A review of this equipment and the test method

is provided in Industrial Diamond Review, March 1974, pp. 133-137. A 20 gram grain sample is prescreened on a Rotap sieve shaker for 15 minutes using 50 and 60 mesh electroformed sieves, equivalent to 322 um and 255 um openings. Approximately 0.36 grams of screened material is then placed in a cylindrical sample capsule together with a 5/16 inch ball. The capsule and ball are fabricated from hardened tool steel. The cycle frequency is set to  $240 \pm 3$  cpm and the sample capsule is subjected to two dimensional oscillations for a fixed number of cycles. Separate samples are run at a fixed number of cycles ranging from 200 to 500. After cycling is completed, the sample is removed and screened on a Rotap shaker for 3 minutes using 60 mesh and 70 mesh electroformed sieves, equivalent to 255 um and 213 um openings. The sample sieve fractions are weighed and the weight percent of the starting sample which is retained on the 60 mesh sieve is determined. For each material, results are reported as either cycle half life, where the number of cycles for 50% retention is determined or a cumulative rating is assigned based on the sample retention for a series of fixed cycles.

Triple impact toughness is measured on a modified impact mill using a technique developed at Norton Co. The test equipment consists of a conventional impact mill equipped with variable speed rotating paddles with vacuum seals and vacuum port so that the mill chamber can be evacuated to pressure of 0.5 torr with a roughing pump. Grain samples are prescreened to a nominal 35 to 40 grit sizing. Prior to testing, a sample screen analysis is performed on a Rotap sieve shaker for 10 minutes. For the initial test cycle, a nominal sample size of 140 grams is processed in the mill. The mill is sealed and evacuated. When the chamber pressure reaches 0.5 torr, the paddle motor is activated and rotation is increased to 3000 rpm. When the paddle speed has stabilized, the sample is slowly fed into the chamber where it impacts

the paddle blade and rebounds into a sample collection chamber. After the entire sample is processed, a screen analysis is repeated on the Rotap and the weight for two cumulative U.S. screen fractions, -40/+50 and -40/+70, are reported as a fraction of the total sample weight. A single impact toughness rating,  $K_1$  is obtained from averaging the weight fraction of fines remaining from the -50 and -70 sieve fractions. A screened -40/+45 sample fraction from the first impact cycle is then recycled through the impact mill and a screen analysis is repeated on the impacted material. The screening results from this second impact cycle are again analyzed and the impact toughness is reported as a  $K_2$  value. The process is repeated a third time with the -40/+45 screen fraction from the second impact cycle and a  $K_3$  impact toughness value is reported. The  $K_1$  value is generally recognized as being heavily influenced by grain shape, whereas, the  $K_3$  value is thought to represent the intrinsic properties of the grain. In all cases, a lower K value indicates a higher grain impact toughness.

The compressive strength of spherical or cylindrical shaped grains was measured by either diametrical compression (Roark's Formulas for Stress and Strain, 6th edition, W.C. Young (ed.), McGraw-Hill, New York, 1989, p. 650, or the Brazilian Disk Test (F.Carniero and A.Barcellos, Union of Testing and Research Laboratories for Materials and Structures, No. 13 (1953)). Individual grain samples are placed between two tungsten carbide flats and the sample is compressed on a Model 4206 Instron (Instron Corp. Canton, MA) at a constant cross head speed of about 0.5 mm/min as a uniaxial compressive load is applied. The applied load is recorded as a function of ram displacement until the sample fractures. The mean maximum compressive stress, strain to failure and compressive modulus is determined for an average of from ten to twenty five samples.

Indentation hardness was measured on mounted and

polished grain cross sections with a Vickers indenter and a Leco DM-400 Microhardness machine, available from Leco Corp. of St. Louis, Mo., using a 200 gram load.

5 The indentation fracture toughness of individual grains was measured on mounted and polished grain cross sections with a Vickers indenter and a Leco DM-400 Microhardness machine using a 500 gram load.

Vitrified grinding wheels were produced which incorporated the sintered silicon carbide grain as a  
10 direct substitute for conventional silicon carbide grain with no further modification of the wheel formulation. The wheels comprised between 8 and 9 volume percent of a high temperature glass bond and 48 volume percent of 46 grit abrasive, the remainder being porosity. A 5 inch  
15 o.d., 1.25 inch i.d. by 0.5 inch thick wheel size was utilized for these tests.

The standard sandblast penetration test was followed: Approximately 50 cc of round Ottawa spherical sand, sieved to a -U.S. 24/+ U.S. 30 size fraction, is  
20 charged to a small sandblast feed hopper. The sand is fed through a 3/16 inch i.d. boron carbide nozzle at an air pressure of 15 psig and feed rate of about 8 cc/sec so as to impinge on a vitrified test sample. After a six second sandblast exposure, the surface of the the sample  
25 is cleaned with an air blast for 4 seconds and the depth of surface recession from the penetration of the sandblast is measured with a dial indicator. The average of two measurements is reported.

For the MOR (strength) test, a 4.0 inch by 1.0 inch  
30 by 0.5 inch thick test bar is placed on a 4 point loading fixture with a 1 inch top span and a 3 inch bottom span. The fixture is place on an Model 1125 Instron tester (Instron Corp., Canton, MA), and the test bar is loaded at a cross head speed of 0.050 inches/min until failure.  
35 Modulus of rupture is calculated from averaging the maximum load measured at the point of failure for five test bars.

For the modulus of elasticity test, a model MK5 Industrial Grindo-Sonic acoustical instrument (J.W. Lemmens Inc., St. Louis, MO) was utilized for elastic modulus measurements of test materials. A 4.0 inch by 1.0 inch by 0.5 inch thick test bar is supported on a knife edge fixture with the two knife edges spaced at points of minimum vibration which are located approximately 1/5 of the length away from the test bar ends. An acoustic transducer probe is placed adjacent to the middle of the bar and the sample is tapped lightly with a nylon hammer. Three measurements are made of the resonant frequency of the sample. The modulus of elasticity is calculated from measurement of the sample dimension, weight, density and frequency, where  $MOE = (L^4 f^2 \cdot \text{density}) / (0.975 \cdot t^2)$ .

The grinding performance of vitrified wheels produced with grains of the present invention was compared with vitrified wheels produced with conventional silicon carbide grain in grinding tests on nodular cast iron, titanium and tungsten carbide. Vitrified wheel grinding tests were performed on a Brown and Sharpe Model 818 surface grinder, available from Brown and Sharp Mfg. Corp., of North Kingston, RI, using a wheel speed of 4965 rpm equivalent to 6500 sfpm. A workpiece table translation speed of either 30 ft/min or 50 ft/min was utilized. A 5% aqueous solution of Trim Clear rust inhibitor (Master Chemical Corp., Perrysburg, OH) was used in wet grinding tests.

The performance and effectiveness of an abrasive article is typically evaluated in grinding tests where the rate of wear of the abrasive material and workpiece, the power consumption for material removal, the grinding force, translation speed of the workpiece, rotational speed of the wheel, and workpiece surface finish is measured. Typically, the grinding ratio, or "G-Ratio", defined as the volumetric ratio of workpiece material removal to abrasive product wear, is used to characterize

the performance of an abrasive product. The grinding ratio measures the durability of an abrasive article in grinding a particular material. Typically, a superior abrasive article will possess a higher grinding ratio at equivalent or higher workpiece removal rates than an inferior article. In addition, a superior abrasive article will maintain a high grinding ratio with increasing down feed and workpiece removal rates. Another criterion for characterizing the performance of an abrasive product is workpiece surface finish. A superior abrasive article will produce a lower surface roughness on a ground workpiece when compared to an inferior abrasive article made with an equivalent grit size.

#### EXAMPLE I

A silicon carbide sinterable formulation was prepared by mixing 1.18 kg of a phenolic resol resin (Borden Al-5614), 0.32 kg of boron carbide (Stark HS), 25 kg of deionized water, 0.5 kg of polyethylene glycol (Carbowax 400), 25 kg of silicon carbide powder (Norton FCP-15) and 5 kg of silicon carbide milling media in a jar mill. The pH of the mixture was adjusted to 9.0 with ammonium hydroxide and the formulation was roll milled for 16 hours. The viscosity and pH of the mixture were measured after milling, and the solids content and pH were adjusted as necessary prior to spray drying. The mixture was then spray dried using Niro Type HT portable spray dryer (Niro Inc., Columbia, MD) to a final moisture content of between 0.5 to 2.0%. A free-flowing powder was produced from the spray dried formulation which consisted of spherical aggregates ranging in size between 2  $\mu$ m to 300  $\mu$ m. The resultant spray dried powder formulation was used as a feed material for Examples I through V and Examples VII through VIII.

Approximately 30 kg of spray dried silicon carbide powder formulation was charged to an Eirich R07 mixer (Eirich Machines Inc., Maple, Ontario, Canada) equipped

with a pelletizing rotor blade. 1.125 kg of Goshenol KH17S PVA (Nippon Gohsei, Osaka, Japan) was added to the mixer and dry mixed with the powder formulation at low speed. With the mill operating at low speed, 5.0 kg of  
5 a water-methanol solution (50/50 weight percent) was aspirated and sprayed onto the solid charge during mixing. The mill speed was increased and adjusted to provide for formation of small, uniform spherical pellets through agglomeration of the powder charge. Typically,  
10 pellet sizes ranged between 300 to 2000  $\mu\text{m}$  with a peak distribution between 500 to 1000  $\mu\text{m}$ . The pellet density was between 1.5 to 1.8  $\text{g}/\text{cm}^3$ .

The green pellets were dried overnight in a convection oven at 110°C prior to firing. The pellets  
15 were subsequently pressureless sintered as follows. Green pellets were heated at a rate of 15°C per minute to 1500°C under a vacuum ranging from less than 0.001 torr to 100 torr. After holding at 1500°C for 30 minutes under vacuum, the furnace was backfilled with argon gas  
20 to a nominal pressure of 760 torr. The temperature was then increased at a rate of 20°C per minute to 2150°C and held for one hour. After cooling to room temperature, pellet densities were measured by the Archimedes method, by helium pycnometry and by mercury intrusion porosimetry  
25 and ranged between 3.05 to 3.21  $\text{g}/\text{cm}^3$ .

Next, sintered pellets were crushed to appropriate size and shape. An impact mill, equipped with steel paddles and operating at 1300 rpm, was used to attain blocky shaped grains. A roll crusher, with a gap setting  
30 of approximately twice the average diameter of the targeted grit size, was used to attain weak shaped grains. Grit sizing was obtained by screening through conventional polyester or stainless steel mesh sizes to either ANSI, FEPA or CAMI standard grit sizes. For small  
35 grain batches, an 18 inch Sweco Vibro-energy Separator, manufactured by Sweco Inc. of Florence, KY, was used for screening. For large grain batches, a 4 sq. ft. Rotex



screener, manufactured by Rotex Inc. of Cincinnati, OH, was used.

The physical and mechanical properties of the impact milled, blocky shaped, sintered silicon carbide grain produced by this method are compared to conventional silicon carbide grain in Figure 4. The mechanical properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and 6. The grain properties, wheel properties and grinding performance data set forth in Figures 4-6 were drawn from blocky grain embodiments of Examples I-IX of the present invention.

#### EXAMPLE II

A sinterable silicon carbide powder formulation was spray dried and pelletized according to the procedure identified in Example I. The green pellets were dried overnight in a convection oven at 110°C prior to crushing. The dried pellets were crushed to appropriate size using either an impact mill for blocky shaped grain or a roll crusher for weak shaped grain. Grit sizing was achieved by screening to ANSI, FEPA or CAMI standard grit sizes using either a Sweco or Rotex screener. The green, unfired grain was classified to approximately 20% oversize in order to accommodate the shrinkage which occurs during sintering.

The green, crushed and classified grain was subsequently sintered for 1 hour at 2150°C following the firing cycle of Example I. Fired densities were measured by the Archimedes method, by helium pycnometry and by mercury intrusion porosimetry and ranged between 3.06 to 3.19 g/cm<sup>3</sup>.

Grains produced by the method of this example possessed a unique surface texture which has not been observed in any other abrasive grain material. Figures 1-3 shows the range of surface textures of grains produced by this method where examples of fine, moderate and coarse surface textures, respectively, are shown at

500 X.

The characteristic properties of grains made with this method are provided in Figure 4. The mechanical properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and 6.

### EXAMPLE III

A spray dried sinterable powder formulation was produced according to the procedure identified in Example I. Approximately 500 grams of spray dried powder blend was charged to a 6" by 6" square mold and uniaxially pressed at 2000 psi ram pressure. The resultant pressed brick was removed from the mold, sealed in a polyethylene bag and placed in an Isomax-30 cold isostatic press (National Forge Co., Irvine, PA). The die pressed brick was then pressed at 30,000 psi under isostatic conditions to a green density of between 1.6 to 2.0 g/cm<sup>3</sup>. The isostatically pressed brick was removed from the polyethylene bag and stored in a drying oven at 110°C.

The green bricks were dried overnight at 110°C prior to firing. The bricks were subsequently sintered for 1 hour at 2150°C following the firing cycle of Example I. Fired densities were measured by the Archimedes method, by helium pycnometry and by mercury intrusion porosimetry and ranged between 3.13 to 3.17 g/cm<sup>3</sup>.

Sintered bricks were crushed in a jaw crusher to a nominal 1/4" sizing and fed to either an impact mill for "blocky" shaped grain or a roll crusher for "weak" shaped grain. Grit sizing was obtained by screening crushed grain through polyester or stainless steel screens to either ANSI, FEPA or CAMI standard grit sizes using a Sweco screener.

The characteristic properties of grains made with this method are provided in Figure 4. The mechanical properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and 6.

## EXAMPLE IV

This Example is a prophetic Example. Cold isostatically pressed powder bricks are processed according to the procedures of Example III. After drying  
5 overnight at 110°C, the bricks are crushed to a nominal 1/4" sizing and fed to either an impact mill for "blocky" shaped grain or a roll crusher for "weak" shaped grain. Grit sizing is achieved by screening crushed grain through ANSI, FEPA or CAMI standard screen mesh sizes  
10 using either a Sweco or Rotex screener. The green grain is classified to approximately 20% oversize in order to accommodate the shrinkage which occurs during sintering.

The green crushed and classified grain is subsequently sintered for 1 hour at 2150°C following the  
15 firing cycle of Example I. As is observed in Example II above, grains produced by this example will possess a unique surface texture which has not been observed in other abrasive grain materials.

## EXAMPLE V

A spray dried sinterable powder formulation was produced according to the procedure identified in Example I. Approximately 700 grams of spray dried powder blend  
5 was charged to a 6" by 6" graphite hot press mold cavity. The powder was tamped for improved packing and covered with a graphite spacer. A total of nine successive layers of powder and mold spacers were placed in the mold cavity. The mold assembly was placed in a uniaxial press  
10 and pressed at 300 psi for compaction at room temperature. Additional powder was charged as was needed to the mold cavity and the mold assembly was compacted again at 300 psi.

The mold assembly was placed in a vacuum hot press  
15 furnace, approximately 300 psi ram pressure was applied to the mold, and the furnace was evacuated, backfilled with argon and re-evacuated at room temperature. The furnace was then heated to 1800°C as the ram pressure was increased from 300 psi to 3000 psi. The ram pressure was  
20 held constant at 3000 psi as the temperature was raised to 2075°C. The furnace was held at 2075°C for 30 minutes at which time the power was turned off and the furnace was cooled to room temperature.

The hot pressed plates were crushed in a jaw crusher  
25 to a nominal 1/4" sizing and fed to either an impact mill for "blocky" shaped grain or a roll crusher for "weak" shaped grain. Grit sizing was obtained by screening crushed grain through polyester or stainless steel screens to either ANSI, FEPA or CAMI standard grit sizes  
30 using a Sweco screener.

The characteristic properties of grains made with this method are provided in Figure 4. The mechanical properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and  
35 6.

## EXAMPLE VI

A silicon carbide sinterable formulation was

prepared by mixing 6.5 kg of sub-micron silicon carbide powder (Norton FCP-15), 6.5 kg of 2-3 micron silicon carbide powder (Norton E277), 0.13 kg of Black Pearls 1300 carbon black (Cabot Corp., Billerica, MA), 0.13 kg  
5 of BO-250 amorphous boron powder (Atlantic Equipment Engineers, Bergenfield, NJ) and 6.5 kg of deionized water in a jar mill for 72 hours. The mill batch was then freeze dried using a Unitop 200/Freezemobile 6 laboratory  
frieze drier (The Virtis Co., Gardiner, NY). The dried  
10 formulation was crushed and sieved through a U.S. 80 mesh screen prior to use.

An extrusion formulation was prepared by mixing 9 kg of the frieze dried powder blend, 0.138 grams of Methocel A4M (Dow Chemical Co., Midland, MI), 180 grams of  
15 Sorbitol (Lonza Inc., Fair Lawn, NJ) and 1.94 kg of distilled water in a sigma blade mixer. The mixture was kneaded for approximately 2 hours in an Abbe MP sigma-blade mixer (Paul O. Abbe Inc., Little Falls, NJ) to produce an extrudable mix consistency.

20 This formulation was then extruded with a piston extruder equipped with a 20RT electro-plated perforated plate die (Stork Veco International, Bedford, MA). This die had a nominal thickness of 0.018 inches, an 8% open area and hole sizing of 0.012 inches. The extrusion  
25 formulation was placed in the extruder bore and pre-compressed under vacuum for degassing the mix. During extrusion, the piston ram pressure was adjusted between 500 to 5000 psi. The extrudate was dried overnight at 140°C and was then partially crushed to increase bulk  
30 density prior to firing.

The dried extrudate was then sintered at 2150°C for 1 hour following the firing cycle of Example I. The fired density was measured using both Archimedes method and helium pycnometry and ranged between 3.05 to 3.19  
35 g/cm<sup>3</sup>. The sintered extrudate was fractured on an impact mill equipped with steel paddles rotating between 350 to 500 rpm in order to produce cylindrical-shaped grain with

a controlled aspect ratio. The fractured extrudate was classified to a nominal aspect ratio of 2.0 taking a -US 35/+US 100 fraction screened with an 18 inch Sweco Vibro Energy Separator.

5       The characteristic properties of grains made with this method are provided in Figure 4. The mechanical properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and 6.

10

## EXAMPLE VII

A spray dried sinterable powder formulation was produced according to the procedure identified in Example I. An extrudable formulation was prepared from 1 kg of this powder blend which was mixed in a jar roll mill  
15       overnight with 10 grams of laboratory grade stearic acid (Sargeant-Welch Scientific Co., Skokie, IL), 20 grams of Goshenol KH17S PVA, 10 grams of Sorbitol and 480 grams of distilled water. The mixture was dried at 150°C overnight, then crushed and screened through a U.S. 80  
20       mesh sieve.

Approximately 90 grams of the dried extrusion mixture was charged to a 3" by 3" square mold and tiles were uniaxially pressed at 2000 psi ram pressure. The resultant pressed tiles were removed from the mold,  
25       sealed in a polyethylene bag and placed in a cold isostatic press. The die pressed tiles were then pressed at 30,000 psi under isostatic conditions to a green density of between 1.6 to 1.8 g/cm<sup>3</sup>. The isostatically pressed tiles were removed from the polyethylene bag and  
30       stored in a drying oven at 110°C overnight. The tiles were subsequently sintered for 1 hour at 2150°C following the firing cycle of Example I. Fired densities were measured by the Archimedes method and ranged between 3.12 to 3.16 g/cm<sup>3</sup>.

35       Samples of the extrudable mixture were prepared for extrusion and measurement of mix rheology. Approximately 90 grams of a sinterable silicon carbide formulation

prepared according to the method identified in Example I was mixed with 0.9 grams of stearic acid, 1.8 grams of Goshenol K17S PVA, 0.9 grams of Sorbitol and 18 grams of distilled water in a Brabender Plasti-Corder (Brabender Instruments Inc., South Hackensack, NJ) equipped with a sigma-blade mixing head. Samples of this mix were extruded through both 0.0826 inch diameter and 0.0144 inch diameter orifices using a Kayness Galaxy IV capillary rheometer (Kayness Inc., Honeybrook, PA). The extrudate was dried overnight at 150°C prior to sintering. The dried extrudate was sintered at 2150°C for 1 hour following the firing cycle of Example I. The fired density was measured using both Archimedes method and helium pycnometry and ranged between 3.05 to 3.21 g/cm<sup>3</sup>.

#### EXAMPLE VIII

A sinterable powder slurry formulation was produced according to the procedure identified in Example I. A nominal 50% solids slurry was processed in a Niro HT spray drier using a 50 mm AR centrifugal atomizer wheel operated at 40,000 rpm. The inlet drying air temperature was set at 280°C with a flowrate of 70 kg/hr. The outlet air temperature was maintained between 90°C and 100°C and the powder slurry was dried to a moisture content of between 0.88 and 1.35% at a throughput rate of approximately 10 kg/hr. The resultant product consisted of green spherical aggregates with a mean diameter, or  $d_{50}$ , of approximately 25  $\mu\text{m}$ . The mean powder aggregate size and  $d_{50}$  was controlled over the range of 10  $\mu\text{m}$  to 60  $\mu\text{m}$  through adjustment of the slurry viscosity, solids loading or rotation speed of the atomizing wheel.

The remainder of this Example is a prophetic Example. The green atomized powder aggregates are sintered at 2150°C for 1 hour following the firing cycle of Example I. The sintered aggregates are jet milled for crushing to final size and shape and the processed material is then classified by either a sedimentation

method or air classification to grain sizes which range between FEPA P240 to P1200 microgrit standards.

#### EXAMPLE IX

A silicon carbide sinterable formulation was prepared by mixing 1.43 kg of a phenolic resol resin (Borden Al-5614), 0.51 kg of boron carbide (Stark HS), 10 kg of deionized water, 0.2 kg of polyethylene glycol (Carbowax 400), 10 kg of silicon carbide powder (Norton FCP-15) and approximately 2 kg of silicon carbide milling media in a jar mill. The pH of the mixture was adjusted to 9.0 with ammonium hydroxide and the formulation was roll milled for 16 hours. The viscosity and pH of the mixture were measured after milling, and the solids content and pH were adjusted as necessary prior to spray drying. The mixture was then spray dried using a Niro Type HT portable spray dryer (Niro Inc., Columbia, MD) to a final moisture content of between 0.5 to 2.0%. A free-flowing powder was produced from the spray dried formulation which consisted of spherical aggregates ranging in size between 2 um to 300 um. The resultant spray dried powder formulation was used as a feed material for this example.

Approximately 10 kg of spray dried silicon carbide powder formulation was charged to an 20 liter Lödige horizontal mixer (Little Bros. Inc., Florence, KY) equipped with a pelletizing rotor blade. Approximately 0.375 kg of Goshenol KH17S PVA was added to the mixer and dry mixed with the powder formulation at low speed. With the mill operating at low speed, approximately 2.5 kg of a water-methanol solution (50/50) was aspirated and sprayed onto the powder charge during mixing. The mill speed was increased and adjusted to provide for formation of small, uniform spherical pellets through agglomeration of the wet powder. Typically, pellet sizes ranged between 300 to 5000 um with a peak distribution between 1000 to 3000 um. The pellet density was between 1.5 to 1.8 g/cm<sup>3</sup>.



The green pellets were dried overnight in a convection oven at 110°C prior to firing. The pellets were subsequently pressureless sintered at 2150°C for 1 hour following the firing cycle of Example I. Pellet densities were measured by the Archimedes method, by helium pycnometry and by mercury intrusion porosimetry and ranged between 3.05 to 3.21 g/cm<sup>3</sup>. Sintered pellets were crushed to appropriate size for testing using a Sturtevant laboratory roll mill. Sizing to 46 Grit was obtained on a Model B, Ro-Tap Testing Sieve Shaker (W.S.Tyler Inc., Gastonia, NY) equipped with U.S. screens. Indentation toughness, Vickers indentation hardness and DeBeers friability tests were performed on grain samples and the results are reported in Figure 4.

15

## COMPARATIVE EXAMPLES

In order to compare the grains of the present invention to those of the prior art, two types of conventional silicon carbide grains, green CRYSTOLON 39C manufactured by Norton A/S in Lillesand, Norway, and black CRYSTOLON 37C grains manufactured by Norton Company of Worcester, Massachusetts, were tested in the same manner as the above examples. The characteristic properties of these grains are provided in Figure 4.

As set forth in Figure 4, the results of grain characterization tests indicate that the grains of the present invention exhibit superior properties as compared to the prior art. Comparing the comparative examples to the embodiments of the present invention reveals that grains of the present invention display superior hardness, toughness, compressive strength and modulus.

The mechanical properties of vitrified grinding wheels made with the grains of the Comparative Examples are provided in Figure 5. In comparing the mechanical properties of vitrified wheel materials made from the comparative examples with the embodiments of the present invention, vitrified composite materials of the present invention display superior wear resistance (hardness),

strength (modulus of rupture), and modulus of elasticity.

The grinding performance of vitrified grinding wheels made with the grains of the Comparative Examples are provided in Figure 6. Comparing grinding test results of the comparative examples to the embodiments of the present invention reveals that the present invention displays superior grinding ratios, metal removal rates and workpiece surface finish. In particular, the abrasive articles having sintered, shaped polycrystalline SiC grains of the present invention typically have grinding ratios significantly higher than abrasive articles made from conventional monocrystalline SiC grains, thus indicating high durability. In addition, as shown by the data of Figure 6, abrasive articles having grains of the present invention maintain high grinding ratios at increased cutting rates. Further, the workpiece surface finish obtained with abrasive articles containing grains of the present invention is also superior to the finish obtained with conventional SiC grains. These grinding results demonstrate very clearly that the performance of sintered, shaped polycrystalline SiC grains of the present invention is superior to that of conventional monocrystalline SiC grains.

The results reported above indicate that the grains of the present invention exhibit substantially superior performance over conventional silicon carbide grains in abrasive applications. Without wishing to be tied to a theory, it is believed that the superior performance can be attributed to the microcrystalline structure and shape of the sintered polycrystalline grains as well as the absence of inclusions and intrinsic defects such as cracks or dislocations. In particular, the microcrystalline nature of the grains should provide an intrinsically tougher grain than the prior art alpha-SiC monocrystal grain since intergranular fracture and crack propagation proceed less easily in a polycrystalline grain than transgranular fracture and crack propagation

in a mono-crystalline grain. Furthermore, in consideration of the unique surface texture which is provided with abrasive grains produced by the method of the present invention, it is believed that the superior  
5 mechanical properties and grinding performance in an abrasive article can be attributed to an improved bonding of the grain to the matrix phase which produces an abrasive article with improved strength, stiffness, hardness and wear resistance.

## I Claim:

1. A sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon.
2. The grain of claim 1 having an indentation fracture toughness of at least  $2.0 \text{ MPa}\cdot\text{m}^{1/2}$ .
3. The grain of claim 2 having an indentation fracture toughness of at least  $2.5 \text{ MPa}\cdot\text{m}^{1/2}$ .
4. The grain of claim 1 having a compressive strength of at least about 15,000 psi.
5. The grain of claim 1 having a compressive strength of at least about 20,000 psi.
6. The grain of claim 1 having a compressive strength of at least about 75,000 psi.
7. The grain of claim 1 having a compressive modulus of at least about  $5 \times 10^6$  psi.
8. The grain of claim 1 having a compressive modulus of at least about  $6 \times 10^6$  psi.
9. The grain of claim 1 having a density of at least about  $3.0 \text{ g/cm}^3$ .
10. The grain of claim 1 having an 200 g indentation hardness of at least about 25 GPa.
11. The grain of claim 1 having a  $K_1$  triple impact toughness of less than about 0.80.
12. The grain of claim 1 having a  $K_1$  triple impact toughness of less than about 0.50.
13. The grain of claim 1 having a  $K_1$  triple impact toughness of less than about 0.26.
14. The grain of claim 1 having a  $K_2$  triple impact toughness of less than about 0.60.
15. The grain of claim 1 having a  $K_2$  triple impact toughness of less than about 0.40.
16. The grain of claim 1 having a  $K_2$  triple impact toughness of less than about 0.20.
17. The grain of claim 1 having a  $K_3$  triple impact toughness of less than about 0.60.
18. The grain of claim 1 having a  $K_3$  triple impact toughness of less than about 0.40.

19. The grain of claim 1 having a  $K_1$  triple impact toughness of less than about 0.21.
20. The grain of claim 1, wherein the mean diameter of the crystallites is between about 1 micron and about  
5 1000 microns.
21. The grain of claim 1, wherein the mean diameter of the crystallites is between about 1 micron and about 20 microns.
22. The grain of claim 1, wherein the mean diameter of  
10 the crystallites is between about 1 micron and about 5 microns.
23. The grain of claim 1 having a mean surface roughness of less than about 2 microns.
24. The grain of claim 1 having a mean surface roughness  
15 of between about 2 and about 10 microns.
25. The grain of claim 1 having a mean surface roughness of between about 10 and about 20 microns.
26. The grain of claim 1 having a mean surface roughness of more than about 20 microns.
- 20 27. The grain of claim 1 wherein the grain has a shape that is weak.
28. The grain of claim 1 wherein the grain has a shape that is strong.
29. The grain of claim 1 wherein the grain has a  
25 predetermined cross sectional shape which does not vary over its length.
30. The grain of claim 29 where the predetermined cross sectional shape is circular, annular, elliptical, triangular, quadrilateral, diamond, square,  
30 rectangular, trapezoidal, hexagonal, pentagonal, corrugated or hollow.
31. The grain of claim 29 wherein the grain has an aspect ratio of between about 1.0 and about 5.
32. The grain of claim 1 wherein the grain comprises  
35 excess carbon.
33. The grain of claim 32, wherein the excess carbon is present of between about 0.1 and about 10.0 weight

percent.

34. The grain of claim 1, wherein the grain comprises boron.
- 5 35. The grain of claim 34, wherein the boron is present of between about 0.1 and about 30 weight percent.
- 10 36. The grain of claim 1 comprising a sintering aid selected from the group consisting of CaO, MgO, BaO, alkaline earth oxides, transition metal oxides, rare earth oxides, alumina, silica, phosphate compounds, borate compounds, metals, metal carbides, borides, aluminides, silicides, and phosphides.
- 15 37. A process for producing a textured, sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon, comprising the sequential steps of:
- 20 a) forming a shape from a formulation comprising silicon carbide powder and at least one sintering aid,
- b) crushing the shape to produce non-spherical silicon carbide grains, and
- 25 c) sintering the non-spherical silicon carbide grains in the absence of free silicon.
38. The process of claim 37, wherein the shape is formed by agglomeration.
- 25 39. The process of claim 37, wherein the shape is formed by extrusion.
40. The process of claim 37, wherein the shape is formed by cold isostatic pressing.
- 30 41. The process of claim 37, wherein the shape is formed by injection molding.
42. The process of claim 37, wherein the shape is formed by slip casting.
43. The process of claim 37, wherein the shape is formed by tape casting.
- 35 44. A process for producing a sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon, comprising the sequential steps of:

- a) forming a shape from a formulation comprising silicon carbide powder and at least one sintering aid,
- b) sintering the shape in the absence of free silicon, and
- c) crushing the shape to produce non-spherical silicon carbide grains.
45. The process of claim 44, wherein the shape is formed by agglomeration.
46. The process of claim 44, wherein the shape is formed by extrusion.
47. The process of claim 44, wherein the shape is formed by cold isostatic pressing.
48. The process of claim 44, wherein the shape is formed by injection molding.
49. The process of claim 44, wherein the shape is formed by slip casting.
50. The process of claim 44, wherein the shape is formed by tape casting.
51. The process of claim 44, wherein the shape is formed by hot pressing.
52. An abrasive product comprising the abrasive grain of claim 1.
53. The abrasive product of claim 52 comprising a grinding wheel.
54. A silicon carbide grinding wheel having a standard sandblast penetration of less than about 2.5 mm.
55. The grinding wheel of claim 54 having a sandblast penetration of less than about 2.0 mm.
56. The grinding wheel of claim 54 having a sandblast penetration of less than about 1.0 mm.

57. A silicon carbide grinding wheel having an MOR strength of at least about 1850 MPa.
58. The silicon carbide grinding wheel of claim 57 having an MOR strength of at least about 2000 MPa.
- 5 59. The grinding wheel of claim 57 having an MOR strength of at least about 2500 MPa.
60. A silicon carbide grinding wheel having a bond content of about 9% and grinding ratio of at least about 0.5, when wet grinding titanium at a downfeed of 0.3 mils.
- 10 61. The grinding wheel of claim 60 having a metal removal rate of at least about 0.002 in<sup>3</sup>/min.
62. The grinding wheel of claim 60 having a metal removal rate of at least about 0.003 in<sup>3</sup>/min.
- 15 63. A silicon carbide grinding wheel having a bond content of about 9% and a grinding ratio of at least about 20 when dry grinding nodular iron having a Rockwell B hardness of between about 110 and 113 at a downfeed of about 2.0 mils.
- 20 64. The grinding wheel of claim 63 having a metal removal rate of at least about 0.045 in<sup>3</sup>/min.
65. The grinding wheel of claim 63 having a surface finish having a mean roughness of less than about 150 microinches.
- 25 66. A silicon carbide grinding wheel having a bond content of about 9% and a grinding ratio of at least about 150 when dry grinding nodular iron having a Rockwell B hardness of between about 110 and 113 at a downfeed of about 0.5 mils.



67. The grinding wheel of claim 66 having a metal removal rate of at least about 0.013 in<sup>3</sup>/min.
68. The grinding wheel of claim 66 having a surface finish having a mean roughness of less than about 50 microinches.
69. A coated abrasive article comprising grains of claim 1.
70. A composite article comprising a matrix and grains of claim 1.
71. A composite of claim 70 wherein the matrix comprises a metal.
72. A composite of claim 70 wherein the matrix comprises a ceramic.
73. A composite of claim 70 wherein the matrix comprises an organic polymer.
74. A composite of claim 70 wherein the matrix comprises a glass.
75. A sinterable silicon carbide powder formulation comprising:
- a) a sinterable silicon carbide powder having an average particle size of less than one micron and present in an amount of from about 60 w/o to about 90 w/o of the formulation,
- b) a carbon-based additive present in an amount of from about 6 w/o to about 10 w/o of the formulation, and
- c) a boron-based additive present in an amount of from about 4 w/o to about 30 w/o of the formulation.
76. The formulation of claim 75, where the carbon-based additive is present in an amount of from about 6 w/o to about 8 w/o of the formulation.
77. The formulation of claim 75, where the carbon-based additive is present in an amount of from about 6 w/o to about 7 w/o of the formulation.
78. The formulation of claim 75, further comprising a temporary binder present in an amount of from about 0.1 w/o to about 10 w/o of the formulation.

79. The formulation of claim 75, where the boron-based additive is present in an amount of from about 4 w/o to about 10 w/o of the formulation.
- 5 80. The formulation of claim 75, where the boron-based additive is present in an amount of from about 4 w/o to about 6 w/o of the formulation.
81. The formulation of claim 75, further comprising a temporary binder present in an amount of from about 0.25 w/o to about 5 w/o of the formulation.
- 10 82. A sintered silicon carbide ceramic comprising:  
a) silicon carbide present in an amount of from about 60 w/o to about 90 w/o of the ceramic,  
b) excess carbon present in an amount of from about 6 w/o to about 10 w/o of the ceramic, and  
15 c) boron present in an amount of from about 4 w/o to about 30 w/o of the ceramic, said ceramic having a density of at least about 3.00 g/cm<sup>3</sup>.
83. The ceramic of claim 82, where the excess carbon is present in an amount of from about 6 w/o to about 8 w/o of the ceramic.
- 20 84. The ceramic of claim 82, where the excess carbon is present in an amount of from about 6 w/o to about 7 w/o of the ceramic.
85. The ceramic of claim 82, where at least about 50 w/o of the silicon carbide is present as alpha.
- 25 86. The ceramic of claim 82, where the boron is present in an amount of from about 4 w/o to about 10 w/o of the ceramic.
87. The ceramic of claim 82, where the boron is present in an amount of from about 4 w/o to about 6 w/o of the ceramic.
- 30 88. The ceramic of claim 85, where at least about 75 w/o of the silicon carbide is present as alpha.
89. A process for producing a sintered silicon carbide ceramic comprising the sequential steps of:  
35 a) milling an aqueous slurry of coarse silicon carbide powder at a predetermined pH value of

- between about 6.0 and about 10.0 to reduce the mean particle size of the silicon carbide powder to less than one micron,
- 5        b) adding at least one sintering additive to the aqueous silicon carbide powder slurry,
- c) homogeneously mixing the sintering additive with the aqueous silicon carbide slurry,
- d) drying the milled slurry to a moisture content of less than 30% by weight of the silicon carbide
- 10       powder,
- e) forming a green body from the dried slurry, and
- f) sintering the green body without subjecting the green body to chemical treatments which remove oxygen or other impurities.
- 15    90. The process of claim 89 wherein the milled slurry is dried to less than about 2 w/o of the silicon carbide powder.
91. A process for producing a dense silicon carbide ceramic comprising the sequential steps of:
- 20       a) evacuating a furnace containing a sinterable silicon carbide green body having either a moisture content of at least about 0.2 w/o or an oxygen content of at least about 0.1 w/o to a vacuum of at least about 100 torr,
- 25       b) heating the green body under vacuum to a temperature between about 1000°C and about 1500°,
- c) maintaining the temperature between about 1000°C and about 1500°C for at least 30 minutes under vacuum,
- 30       d) backfilling the furnace with argon gas to atmospheric pressure,
- e) further heating the green body in an argon atmosphere to a temperature between 2000°C and 2200°C,
- 35       f) maintaining the temperature of between 2000°C and 2200°C for at least 15 minutes in an argon atmosphere, and

g) cooling the furnace to room temperature.

92. The process of claim 91 comprising evacuating the furnace to less than about 1 torr.

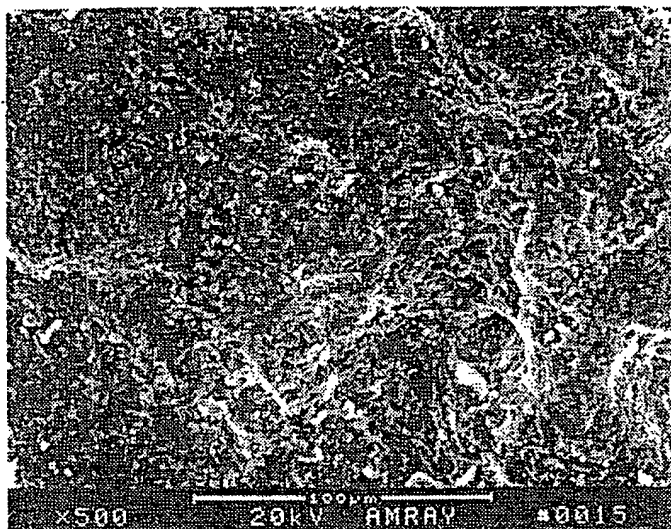


FIG. 1

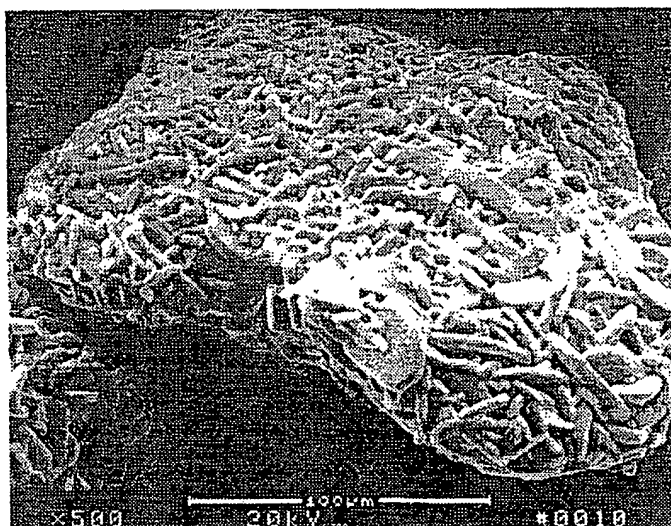


FIG. 2



FIG. 3

EXAMPLE	DENSITY (g/cc)			MEAN CRYSTALLITE SIZE (um)	GRAIN FRIABILITY		TRIPLE IMPACT TOUGHNESS			INDENTATION HARDNESS (GPa)	INDENTATION TOUGHNESS (MPa M <sup>1/2</sup> )	COMPRESSIVE STRENGTH (psi)	COMPRESSIVE MODULUS (Msi)
	H <sub>2</sub> O	He	Hg		YIELD	HALF-LIFE	K1	K 2	K3				
I	3.13	3.21	3.18	1-3	247/400	535	0.26	0.20	0.21	25.2	2.73	75,600	6.0
II	3.06	3.19	3.15	3-6	239/400	478	-	-	-	22.1	2.00	-	-
III	3.15	3.17	3.14	2-4	218/400	450	-	-	-	26.4	2.72	-	-
V	3.17	3.19	3.20	1-3	238/400	463	-	-	-	28.0	1.96	-	-
VI	3.18	3.21	-	2-5	-	-	-	-	-	27.4	-	15,000	0.2
IX	3.09	-	-	1-3	208/400	367	-	-	-	23.6	2.13	-	-
39C	3.14	3.21	-	>>1000	236/400	430	1.07	0.84	0.80	20	1.89	7,000	4.0
37C	3.21	3.21	-	>>1000	246/400	462	-	-	-	22.8	1.79	-	-

FIG. 4

EXAMPLES (46 GRIT)	BOND CONTENT (48 V/O ABRASIVE)	SANDBLAST PENETRATION (mm)	MODULUS OF RUPTURE (psi)	ELASTIC MODULUS (Msi)	DENSITY (g/cc)
I	8%	1.53	2223	33.71	1.694
I	9%	0.98	2811	39.94	1.731
II	8%	2.79	1868	25.74	1.650
II	9%	1.99	—	28.5	1.69
III	8%	2.36	2094	31.27	1.660
III	9%	1.95	2517	35.47	1.702
VI	9%	2.08	—	15.6	1.423
39C	8%	3.48	1599	26.87	1.693
39C	9%	3.16	1291	29.15	1.706
37C	8%	3.47	1460	27.66	1.676
37C	9%	2.16	1748	31.50	1.705

FIG. 5

EXAMPLE (46 GRIT)	BOND CONTENT (%)	DOWN FEED (mils)	AVERAGE PEAK POWER (P)	G-RATIO (G)	METAL REMOVAL RATE (in <sup>3</sup> /min)	WHEEL WEAR RATE (in <sup>3</sup> /min)	SURFACE FINISH (in. x 10 <sup>-6</sup> )
MATERIAL: NODULAR IRON (ROCKWELL B HARDNESS: 110-113), DRY GRINDING							
I	9	0.5	570	187	0.0135	0.00007	42
		1.0	580	268	0.0256	0.00010	55
		2.0	720	182	0.0497	0.00027	99
II	9	0.5	320	174	0.0118	0.00007	63
		1.0	510	186	0.0248	0.00013	82
		1.5	400	110	0.0369	0.00083	90
		2.0	400	29	0.0458	0.00160	130
III	9	0.5	430	153	0.0126	0.00008	47
		1.0	470	179	0.0247	0.00014	63
		2.0	440	87	0.0484	0.00056	108
		2.0	420	40	0.0464	0.00117	130
VI	9	0.5	1040	18	0.0257	0.0014	-
39C	9	0.5	174	111	0.0118	0.00011	69
		1.0	130	4	0.0138	0.00330	110
37C	9	0.5	220	193	0.0126	0.00007	58
		1.0	330	245	0.0240	0.00010	69
		1.5	109	20	0.0328	0.00161	109
		2.0	105	3	0.0240	0.00762	105
III	8	0.5	220	63	0.0119	0.00019	55
		1.0	378	96	0.0242	0.00025	78
		1.5	300	40	0.0349	0.00088	110
		2.0	180	3	0.025	0.00805	109
37C	8	0.5	130	47	0.0113	0.00024	78
		1.0	100	5	0.0147	0.00314	55
MATERIAL: TUNGSTEN CARBIDE (370 CARBOLOY), WET GRINDING							
I	9	0.3	730	0.035	0.0014	0.03984	-
		0.5	760	0.0285	0.0021	0.07343	-
II	9	0.3	480	0.0188	0.0009	0.04721	-
		0.5	520	0.0093	0.0008	0.08191	-
III	9	0.3	480	0.0076	0.0004	0.04931	-
		0.5	550	0.0089	0.0007	0.08389	-
VI	9	0.5	1550	24.69	0.2924	0.0118	-
39C	9	0.5	430	2.9	0.1462	0.0508	-
37C	9	0.3	310	0.0074	0.0004	0.05044	-
		0.5	380	0.0001	0.0	0.08754	-
MATERIAL: TITANIUM, WET GRINDING							
I	9	0.3	260	0.540	0.0019	0.00359	-
II	9	0.3	180	0.290	0.0012	0.00401	-
III	9	0.3	240	0.824	0.0031	0.00373	-
37C	9	0.3	160	0.397	0.0015	0.00389	-

FIG. 6



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/07801

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09K3/14 C04B35/565 B24D3/14		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09K C04B B24D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US,A,4 346 049 (COPPOLA & AL.) 24 August 1982  see claims 1,10 see column 5, line 9 - column 6, line 2  ---	75-81
A		1-36, 82-88
X	EP,A,0 178 753 (KENNECOTT CORPORATION) 23 April 1986  see claims 1-17 see column 7, line 23 - column 8, line 31  ---	82-88
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
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Date of the actual completion of the international search		Date of mailing of the international search report
16 November 1994		24. 11. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer  Rigondaud, B

## INTERNATIONAL SEARCH REPORT

International Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International Application No

PCT/US 94/07801

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